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Crystalline Alternating Sequences Identified in Ethylene-*co*-norbornene Polymers Produced by the $(\eta^5\text{-}C_2B_9H_{11})Zr(NEt_2)_2(NHEt_2)\text{-}Al^iBu_3$ Catalyst

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Ethylene-*co*-norbornene polymers [P(E-*co*-N)s] are novel materials characterized by high thermal stability and interesting optical properties.[1] Reduced light scattering and excellent clarity are expected for copolymers exhibiting homogeneous monomer distribution. A*nsa*-zirconocenes with C_s and C_2 symmetry are scarcely active in norbornene homopolymerization but copolymerize ethylene and norbornene to amorphous random P(E-*co*-N)s.[2−9] Prevailingly isotactic alternating microstructures were obtained with the properly sterically hindered C_1 symmetric zirconocenes of general formula $^iPr[(RCp)Flu]ZrCl_2$[2,7b] and the "constrained geometry catalysts" $Me_2Si(3\text{-}^tBuCp)(adamantylamido)MMe_2$ (M = Zr, Hf).[10] We found that alternating P(E-*co*-N)s can be also produced by the dicarbollide catalysts $(\eta^5\text{-}C_2B_9H_{11})M(NEt_2)_2(NHEt_2)$ (M = Ti or Zr) activated with methylaluminoxane (MAO) or different trialkylaluminum compounds, such as $AlMe_3$, $Al(^iBu_3)$(TIBA), and $AlH(^iBu)_2$.[11] Activation of the group 4 dicarbollides with 10 equiv of TIBA produces catalysts with productivity values greater than the corresponding MAO-activated systems and comparable to that observed for the zirconocene−MAO catalysts. The chemical structure of the active species in these catalysts has not been identified: attempts to isolate the base free dicarbollide alkyl derivatives were unsuccessful because of the thermal instability of these complexes. To gain further insight into dicarbollide-catalyzed ethylene−norbornene polymerization, the behavior of the $(\eta^5\text{-}C_2B_9H_{11})Zr(NEt_2)_2(NHEt_2)$−TIBA (**1**) catalyst has been investigated and preliminarily compared with that of $Me_2Si(3\text{-}^tBuCp)(adamantylamido)ZrCl_2$/MAO (**2**) and $(\eta^5\text{-}C_5Me_5)ZrCl_3$−MAO (**3**): catalyst **2** produces isotactic alternating P(E-*co*-N)s[10] whereas **3** is expected to produce only atactic alternating sequences. The structures of the **1**−**3** precatalysts are shown in Chart 1.

Several ethylene−norbornene copolymerizations were carried out over a wide range of monomer compositions,[12] and the resulting polymer products were analyzed by ^{13}C NMR spectroscopy to gain information about the copolymer microstructure. Selected data for the copolymerization runs and the Fineman−Ross plots are given in the Supporting Information.

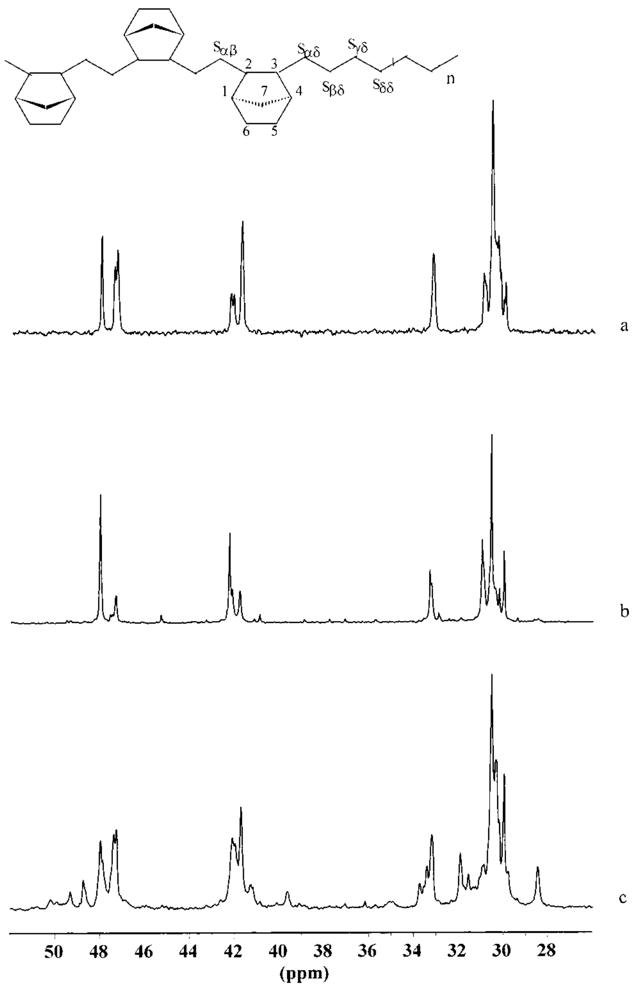

Figure 1. ^{13}C NMR spectra of P(E-*co*-N)s with approximately N mol % = 35 produced by (a) $(\eta^5\text{-}C_2B_9H_{11})Zr(NEt_2)_2(NHEt_2)$, (b) $Me_2Si(3\text{-}^tBuCp)(adamantylamido)ZrCl_2$, and (c) $(\eta^5\text{-}C_5Me_5)ZrCl_3$.

The **1**−**3** catalysts incorporate norbornene through a *cis*-2,3-exo monomer insertion[3] as suggested by the single resonance observed at about 33.3 ppm for the C7 norbornene carbons.[13] At norbornene molar fractions in the feed as high as 1.7 M, the N incorporation in the P[E-*co*-N]s by **1**−**2** catalysts never does exceed 50 mol %, and the copolymers mainly exhibit an alternating structure. The ^{13}C NMR spectrum of the copolymer by **2** catalyst with N mol % = 50 is very simple and exhibits only five resonances at 48.1, 42.4, 33.4, 31.1, and 30.6 ppm that were previously assigned to the alternating erythro-di-isotactic structure.[2,7,8c] On the contrary, the ^{13}C NMR spectrum of the P[E-*co*-N]s with about the same composition (N mol % = 50) by **1**-TIBA catalyst exhibits eight resonances at 48.1, 47.5, 42.4, 41.9, 33.4, 31.1, 30.7, and 30.4 ppm[11] attributed, on the basis of the recent assignments by Tritto et al.,[8] to the isotactic (i-NENEN) and syndiotactic (s-NENEN) alternating monomer pentads with the former slightly prevailing over the other one. (The i-NENEN/s-NENEN intensity ratio of the corresponding signals is about 1.1.) Actually, the signals at 47.5, 41.9, and 30.4 ppm are due to the C2,3 and C1,4 norbornene carbon atoms and $S_{\alpha\beta}$ ethylene carbon atoms of the erythro-di-syndiotactic alternating sequences, respectively, while the signals at 33.3 and 30.7 ppm are due to the C7 and C5,6 of both isotactic and syndiotactic alternating sequences. Moreover, a partial overlap of the C2,3 and C1,4 resonances of the s-NENEN with the same carbons of the EENEE was observed at 47.5 and 41.9 ppm. The **2**−MAO catalyst produces copolymers containing prevailingly i-NENEN sequences, and thus the resonance at 47.2 and 41.8 ppm in the ^{13}C NMR spectrum of a sample

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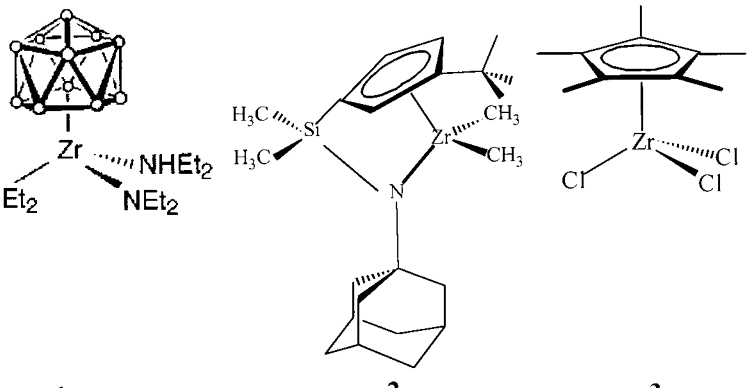
Chart 1



1 **2** **3**

Table 1. Comparison of the Ethylene−Norbornene Reactivity Ratios Determined for 1−3 and Different Zirconium Compounds

catalyst	r_E	r_N	T_P (°C)	ref
$(\eta^5\text{-}C_2B_9H_{11})Zr(NEt_2)_2(NHEt_2)$ (**1**)	1.4	∼0	50	*a*
$\mu\text{-}Me_2Si(3\text{-}{}^tBuCp)$(*N*-adamantylamido)$ZrCl_2$ (**2**)	1.3	0.03	50	*a*
$(\eta^5\text{-}C_5Me_5)ZrCl_3$ (**3**)	27	∼0	50	*a*
rac-$[Et(Ind)_2]ZrCl_2$	1.9	0.03	40	3b
$[Me_2C(Ind)(3\text{-}MeCp)]ZrCl_2$	1.1	0.1	70	7c
$[Me_2C(Flu)(3\text{-}{}^iPrCp)]ZrCl_2$	4.1	0.03	30	16
Cp_2ZrCl_2	4.0	0.03	40	14

[a] This work.

with N mol % = 35 are exclusively due to the C2,3 and C1,4 of the norbornene-centered EENEE pentad. The splitting of the resonance at 47.5 ppm in the ^{13}C NMR spectrum of the sample with approximately the same norbornene composition (N mol % = 39) obtained with **1** catalyst is due to the overlap of the C2,3 norbornene resonance of the s-NENEN with the C2,3 of the EENEE sequence. As previously observed, the intensity of the signal of the i-NENEN pentads is still slightly prevailing over that due to the s-NENEN. The signal at 41.9 ppm does not display such splitting, indicating that the chemical shift difference of the C1,4 in the s-NENEN and EENEE sequences is lower than the spectral line width. The two signals observed in the range 41.5−42.5 ppm are probably due to the C1,4 of the i-NENEN and NENEE sequences.[8,9] The ^{13}C NMR spectrum of the copolymer by **3** catalyst is complicated by the presence of monomer sequences including the NN diad, confirming that unlike the **1**−**2** catalysts the half-sandwich zirconocene is able to homopolymerize norbornene (see Figure 1).

To have a deeper insight into the copolymerization mechanism, we calculated the reactivity ratios r_E ($=k_{EE}/k_{EN}$) and r_N ($=k_{NN}/k_{NE}$) for the **1**−**3** catalysts using the Fineman−Ross method and assuming the monomer concentration in the copolymer corresponding to that calculated from eq 1:

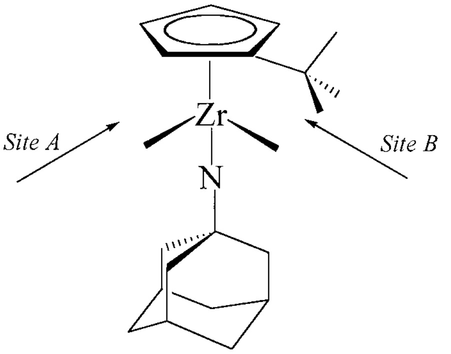
$$\%\ N = \frac{200 I_7}{I_{CH_2}} \tag{1}$$

where I_7 and I_{CH_2} are the area values of the ^{13}C NMR signals due to the norbornene C7 carbon atom and methylene signals appearing in the range 32−28 ppm due to both ethylene and norbornene C5,6 carbon atoms, respectively.

The reactivity ratios determined for **1**−**3** are reported in Table 1 and are compared with those of a number of zirconocenes showing alternating properties in norbornene−ethylene copolymerization.[3b,7c,14,16] The r_E values found for the catalysts **1** and **2** are 1.3 and 1.4, respectively, where the r_N values are close to zero for both catalysts. These results indicate that the ethene or norbornene insertion onto the M−E reactive chain end (M = metal of the active species, E = ethene) occurs with similar probability under the conditions we used, while the formation of the norbornene diads NN is scarcely probable. Data reported in Table 1 are consistent with the tendency for the **1** and **2** catalysts toward alternation, reflected by the observation that even at high norbornene concentration in the feed, the norbornene incorporation is lower than 50 mol % and the NN diad molar concentration is very low. The reactivity values found for **1** and **2** are similar to that observed for the C_1 symmetric zirconocene, showing good alternating properties. On the contrary, the reactivity ratios for the **3**/MAO (r_E = 27 and r_N = 0.008) indicate that the ethylene insertion is strongly favored vs norbornene insertion, and the formation of NN diad is still a not probable event.

The alternating properties of the C_1 symmetric metallocene were previously explained on the basis of an alternating polyinsertion mechanism involving two heterotopic coordination sites.[9] The coordination site hindered by the bulky ^{t}Bu group in the β-position on the Cp ligand exclusively permits ethylene coordination/insertion whereas both ethylene and norbornene can be coordinated/inserted on the other site.

The integral value of the ^{13}C NMR signal at 48.1 ppm was found in fair agreement with the probability to observe the (i-NENEN + $^1/_2$NENEE) pentads value calculated on the basis of the unconditional probability for ethylene (P_E) and norbornene (P_N) insertion, assuming an alternating two-site model.[18] In the case of the constrained geometry catalyst **2**, we found a good agreement between the experimental and theoretical values calculated for the same monomer pentads assuming the same statistics. This means the bulky



N-adamantyl group produces the same steric hindrance of the fluorenyl ligand in the C_1 symmetric metallocene, and the ^{t}Bu group of the Cp ligand induces the same selectivity in the above-described monomer coordination/insertion.

The experimental values measured for the signals at 48.1 and 47.5 ppm in the ^{13}C NMR spectrum of the P[E-*co*-N]s by **1** catalyst due to the C2,3 of the i-NENEN, i-NENEE, s-NENEN, and s-NENEE pentads do not fit with the theoretical values expected from the two site-alternating model. Preliminary experiments suggest that the alternating properties can be anticipated in this case by a first-order Markov statistics in which the last monomer unit in the growing polymer chain controls the incoming monomer unit insertion.[19] The molar concentrations of the i-NENEN and s-NENEN are correctly evaluated only in the samples exhibiting low concentration of isolated norbornene units, namely the EENEE sequence: unfortunately, the overlap of the C2,3 signals due to the s-NENEN and EENEE pentads at 48.0 and 42.3−42.1 ppm and the poor resolution in the region 29−32 ppm corresponding to the ethylene carbons do not permit a sound check of the Markov statistics in the full range of monomer composition.

The DSC heating profile of a typical erythro-di-isotactic alternating P(E-*co*-N) produced with catalyst **2** exhibits in the first heating run a broad endothermic peak at 230 °C corresponding to the melting of the crystalline alternating sequences.[10] After two or more heating runs (10 °C/min; 50−300 °C) the broad peak centered at 230 °C decreases in intensity probably as consequence of the low crystallization rate from the viscous melt.[10] Annealing at 130 °C for 1 h of an amorphous P(E-*co*-N) produced by **2** catalyst with N mol % = 48 produces crystallization of the sample, and endothermic peaks at 160, 206, and 230 °C were actually detected in the first heating run (Figure 2a). The DSC heating profile of P(E-*co*-N) by **1** catalyst displayed in Figure 2b exhibits the same peaks at 150, 200, and 230 °C: thus, despite the ^{13}C NMR spectrum of this sample looks like that expected for an atactic alternating P(E-*co*-N), the comparison of the DSC curves in Figure 2 clearly indicates the presence of isotactic alternating sequences in both the samples. Several peaks in the DSC curves of the of P(E-*co*-N)s produced by **1** and **2** catalysts reveal a further complex polymorphic behavior of these copolymers. The chain conformation of the alternating P(E-*co*-N)s is under investigation by X-ray analysis of samples in fiber form and will be reported in a forthcoming article.

It is worth nothing that the GPC curve of the P(E-*co*-N)s by **1**-TIBA catalyst is monomodal, and the narrow polydispersity of the sample (M_w/M_n = 1.7−2.2) indicates that they arise from a single active species.

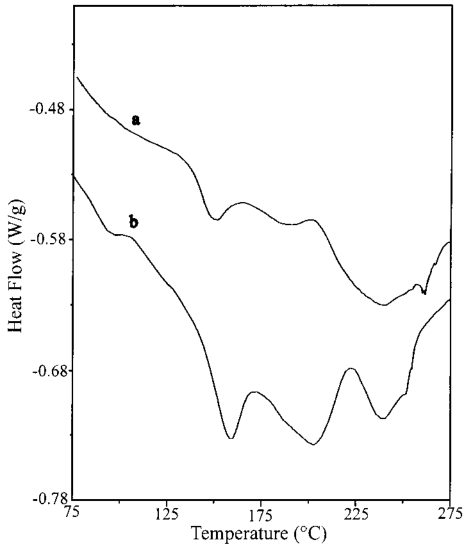


Figure 2. DSC heating profiles of the P(E-*co*-N): (a) with N mol % = 48 produced by **2** and annealed for 1 h at 130 °C and (b) with N mol % = 50 produced by **1**.

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Supporting Information Available: Ethylene/norbornene copolymerization data and Fineman−Ross plots for catalysts **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Copolymers were obtained according to the following standard procedure. A 100 mL flask equipped with a magnetic bar was charged with toluene (40 mL) containing norbornene and Al^{i}Bu$_3$ (for catalyst **1**) or MAO (for catalysts **2**

and **3**). The flask was evacuated and the reactor atmosphere replaced with ethylene at atmospheric pressure: this procedure was repeated three times at 50 °C. After equilibration with ethylene for 15 min, the polymerization was started by injection of the catalyst solution and stopped with 3 mL of methanol acidified with HCl aqueous solution. The copolymer was coagulated in ethanol (200 mL) containing a few milliliters of HCl aqueous solution, recovered by filtration, and dried in high vacuum at 50 °C until constant weight was reached.

(13) The numbering of the carbon atoms is that indicated in the Scheme on the top of Figure 1 and derived from ref 9b.

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(18) In the frame of the alternating polyinsertion mechanism with two heterotopic sites A and B, one (A) permitting exclusively ethylene coordination/insertion and the other one (B) permitting both norbornene and ethylene coordination/insertion, and assuming that the back-skip reaction of the growing polymer chain is slow in comparison to the monomer insertion in both sites A and B, the probability of norbornene and ethylene insertions in the polymer chain is given by $P_{\mathrm{N}} = 1/(r_{\mathrm{E}}F + 1)$ and $P_{\mathrm{E}} = r_{\mathrm{E}}F/(r_{\mathrm{E}}F + 1)$, where $r_{\mathrm{E}} = k_{\mathrm{EE}}/k_{\mathrm{EN}}$ and $F = [\mathrm{E}]/[\mathrm{N}]$ in the feed. Thus, the probability to observe the NENEN and NENEE sequences is given by $P_{\mathrm{NENEN}} = {}^1/_2(1 - P_{\mathrm{E}})^2$ and $P_{\mathrm{NENEE}} = P_{\mathrm{E}}(1 - P_{\mathrm{E}})^2$, respectively (for a more detailed discussion see e.g. ref 9).

(19) In the case of a first-order Markov statistics the probability to observe NENEN and NENEE monomer enchainment is given by $P_{\mathrm{NENEN}} = P_{\mathrm{N}}P^2_{\mathrm{NE}}P^2_{\mathrm{EN}}$ and $P_{\mathrm{NENEE}} = 2P_{\mathrm{N}}P_{\mathrm{NN}}P^2_{\mathrm{NE}}P_{\mathrm{EN}}$, where $P_{\mathrm{N}} = P_{\mathrm{EN}}/(P_{\mathrm{EN}} + 1)$, $P_{\mathrm{NE}} = 1$, and $P_{\mathrm{EN}} = 1/(r_{\mathrm{E}}F + 1)$.

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